

PATENT SPECIFICATION

NO DRAWINGS

1.193.896



Date of Application (No. 26285/68) and filing Complete Specification: 31 May, 1968.

Application made in United States of America (No. 643,047) on 2 June, 1967.

Complete Specification Published: 3 June, 1970.

Index at acceptance:—C3 B(1C6B, 1C6X, 1C8P, 1C12, 1C13M, 1C13P, 1C14A, 1C22, 1C27, 1C28A, 1C28X, 1C33A, 1D1A, 1D1B, 1D2A, 1D2B, 1D2C, 1L6A, 1L6G, 1N1A, 1N6B, 1N6D, 1N13X); B2 K(1A3, 3D, 6A, 7AY, 7A3, 8D, 9F, 9J, 9L, 9P, 9QY, 9Q1, 9Q2, 9Q3, 9Q7, 9Q10); C3 P(10A, 10C2, 10C7, 10C12B, 10C12X, 10C13A, 10C17, 10C20D1, 10C20D3, 10D1A, 10K4, 10K6, 10K7, 10K8, 10K9, 10K10, 10T2A)

International Classification:—C 08 g 30/14

COMPLETE SPECIFICATION

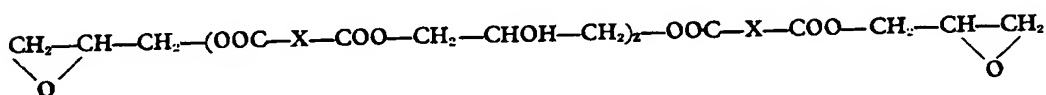
Epoxy Polyvinyl Chloride Resins

- We, CIBA LIMITED, a body corporate organised according to the laws of Switzerland, of Basle, Switzerland, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—
- The present invention relates to epoxy resin compositions for modifying vinyl plastisols and to epoxy resin vinyl chloride compositions.
- Vinyl resins, particularly polyvinyl chloride resins, are widely employed in coating and bonding compositions. Frequently, these resins are employed in the form of solvent free dispersions of the resin in a plasticizer, known as plastisols. Normally, the plastisols also contain conventional ingredients such as pigments, fillers and light and heat stabilisers. Because of the insolubility of the resin particles in the plasticiser at ambient temperature the plastisols form a discontinuous film when applied to a surface. However, when this film is heated the resin particles fuse and a continuous film is formed.
- The nature of the plastisols enables compositions which have an extremely high solids content and which are also mobile and fluid to be obtained. Furthermore, when the resin composition is applied to a surface in the form of a plastisol, films of considerable thickness, of the order of 10—20 mils, can be obtained in a single application. The films obtained after curing have good resistance characteristics, good flexibility and toughness.
- However, the poor adhesion of such vinyl resin compositions to bare metal surfaces has prevented their wide-spread use for metal coating and/or bonding. Various means have been employed to modify the vinyl plastisols and so adapt them for use in the metal fabricating industries. To obtain vinyl resin compositions having improved adhesion to metal surfaces, various substances, including other resins such as the epoxy resins described in United States Patent Specification No. 3,278,477, have been incorporated in the vinyl plastisols. However, none of the modifications so far developed has provided vinyl resin plastisols of satisfactory adhesion to metal surfaces without impairing one or more of the other properties of the composition which are essential in an acceptable coating composition.
- The present invention provides vinyl resin plastisols having satisfactory adhesion to metal surfaces while at the same time retaining those properties essential to the use of such compositions in coating and/or bonding applications.
- It has now been found that an epoxy resin composition comprising a, preferably liquid, epoxy resin, dicyandiamide and benzyl dimethylamine is an effective modifier for vinyl plastisols. The addition of such compositions to vinyl resin plastisols provides a modified vinyl plastisol having excellent solution stability and which may be used to provide films of good colour characteristics, good adhesion properties, excellent flexibility, and good resistance to impact, abrasion and attack by chemicals and hot water.
- Thus the present invention also provides a composition, suitable for coating and/or bonding applications which comprises a dispersion of a vinyl chloride resin in a liquid plasticiser and such an epoxy resin composition.
- By the term "epoxy resin" when used herein is meant an epoxide compound containing more than one 1,2-epoxy group per molecule.

[Price 5s. 0d.]

The epoxide compounds which may be used include esters, for example those obtained by the reaction of a di- or polybasic carboxylic acid with epichlorohydrin or dichlorohydrin in the presence of an alkali. Such polyesters may be derived from aliphatic dicarboxylic acids, such as oxalic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid and sebacic acid, and especially from aro-

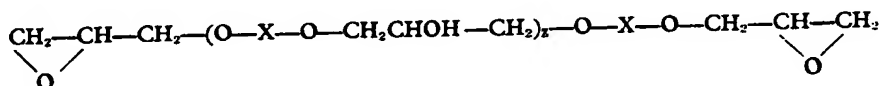
matic dicarboxylic acids, such as phthalic acid, isophthalic acid, terephthalic acid, 2:6-naphthalene-dicarboxylic acid, 2,2'-diphenyl-dicarboxylic acid and ethylene glycol bis-(*para*-carboxy-phenyl)ether. Other esters which may be used include diglycidyl adipate and diglycidyl phthalate, and also the diglycidyl esters of the formula:



in which X represents an aromatic hydrocarbon radical, such as a phenylene radical, and Z represents a small whole or fractional number.

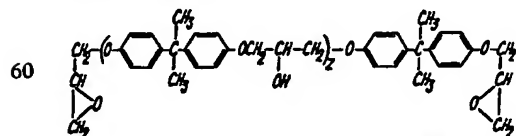
Polyglycidyl ethers may also be used. Such ethers include those obtained by the reaction of a dihydric or polyhydric alcohol or a diphenol or polyphenol with epichlorohydrin or a similar compound such as, glycerol dichlorohydrin, under alkaline conditions or in the presence of an acidic catalyst followed by treatment with alkali. Glycols such as ethylene glycol, diethylene glycol, triethylene glycol, propylene glycol - 1:2, propylene glycol - 1:3, butylene glycol - 1:4, pentane - 1:5 -

diol, hexane - 1:6 - diol, hexane - 2:4:6-triol, glycerine and especially diphenols or polyphenols such as pyrocatechol, hydroquinone, 1:4-dihydroxynaphthalene, 1:5-dihydroxynaphthalene, phenylformaldehyde condensation products, cresolformaldehyde condensation products, bis-(4-hydroxyphenyl)-methane, bis-(4-hydroxyphenyl)-methyl-phenyl-methane, bis(4-hydroxyphenyl)-tolylmethane, 4,4'-dihydroxydiphenyl, bis-(4-hydroxyphenyl)sulphone and preferably 2:2-bis-(4-hydroxyphenyl)propane may be used in the preparation of these polyglycidyl ethers. Ethylene glycol diglycidyl ether and diglycidyl ethers of the formula:



in which X represents an aromatic radical, and Z represents a small whole or fractional number may also be used.

Epoxide resins which are liquid at room temperature are especially suitable, for example, those obtained from 4:4'-dihydroxydiphenyl-dimethylmethane (Bisphenol-A), which have an epoxide content of about 3.8 to 5.88 epoxide equivalents per kilogram. Such epoxide resins have the formula:



in which Z represents a small whole or fractional number, for example, between 0 and 2.

Cycloaliphatic polyepoxides such as those disclosed in United States Patent Specifications Nos. 3,027,357, 3,072,678, 3,147,279 and 3,210,375 may also be used.

The polyvinyl chloride resins referred to herein, may be homopolymers of vinyl chloride or copolymers or interpolymers containing at least 70% by weight of vinyl chloride and

up to about 30% by weight of one or more other vinyl monomers copolymerisable with vinyl chloride. The other vinyl monomers which may be included with the essential vinyl chloride in the polyvinyl chloride resins for the purposes of this invention are those monomers having a



group. Such monomers include other vinyl halides such as vinyl bromide, vinyl fluoride, vinylidene chloride, vinylidene bromide, vinylidene fluoride, chlorotrifluoroethylene, 1,2-dichloroethylene, and tetrafluoroethylene; vinyl esters such as vinyl acetate, vinyl propionate, vinyl butyrate, vinyl benzoate, vinyl laurate, isopropenyl acetate and isopropenyl caproate; acrylate and methacrylate esters such as methyl acrylate, ethyl acrylate, propyl acrylate, isopropyl acrylate, the butyl acrylates, the amyl acrylates, the hexyl acrylates, the heptyl acrylates, the octyl acrylates, the dodecyl acrylates, phenyl acrylate, cyclohexyl acrylate, methyl methacrylate, ethyl methacrylate, the propyl methacrylates, the butyl

- methacrylates, the amyl methacrylates, the hexyl methacrylates, the heptyl methacrylates, the octyl methacrylates, the nonyl methacrylates, the decyl methacrylates, the dodecyl methacrylates, phenyl methacrylate and cyclohexyl methacrylate; maleate and fumarate esters such as diethyl maleate, the dipropyl maleates, the dibutyl maleates, the diamyl maleates, the dihexyl maleates, the dioctyl maleates, the dilauryl maleates, dimethyl fumarate, diethyl fumarate, the dipropyl fumarates, the dibutyl fumarates, the diamyl fumarates, the dihexyl fumarates, the diheptyl fumarates, the dioctyl fumarates, the didecyl fumarates, dicyclohexyl fumarate and diphenyl fumarate; vinyl aromatic monomers such as styrene, alpha-methyl styrene, the vinyl toluenes, the vinyl xylenes and vinyl naphthalene; monoolefins such as ethylene, propylene, the butylenes, the amylenes, the hexylenes and cyclohexene, the vinyl ethers such as vinyl methyl ether, vinyl ethyl ether, the vinyl propyl ethers, the vinyl butyl ethers, the vinyl amyl ethers, the vinyl hexyl ethers, the vinyl heptyl ethers, the vinyl octyl ethers, vinyl cyclohexyl ether, vinyl phenyl ether and vinyl benzyl ether; allyl esters and ethers such as allyl acetate, allyl laurate, allyl benzoate, allyl methyl ether and allyl ethyl ether; vinyl cyanides such as acrylonitrile, methacrylonitrile, and vinylidene cyanide.
- The preferred vinyl resin is a high molecular weight polyvinyl chloride resin having a molecular weight of about 20,000 to 30,000 as measured by the Staudinger method. The resin preferably has a particle size of 44—74 microns (325—200 mesh).
- The plasticiser in which the vinyl resin is dispersed can be any one of the plasticisers conventionally used in forming plastisols. Examples of useful plasticisers include di - 2 - ethylhexyl phthalate, tricresyl phosphate, dicapryl phthalate, butyl esters of acetylated polymerised ricinoleic acids, dibutoxyethyl phthalate, tri - 2 - ethyl - hexyl phosphate, methoxy - ethyl - acetyl ricinoleate, triethylene glycol di - 2 - ethyl hexoate and triethylene glycol esters of coconut oil fatty acids. Examples of useful resinous plasticisers include epoxidised oils and polyesters. Other suitable plasticisers include butyl phthalate, butyl glycolate, dibutyl phthalate, diamyl or dibutyl sebacate, di - 2 - ethyl hexyl sebacate, and tributyl phosphate. A mixture of plasticisers, both of the resinous and of the solvent type can also be employed.
- We have also found it is advantageous to include in the composition to be used for coating small amounts of heat and light stabilisers such as organo-metal complexes, calcium, cadmium or lead soaps, calcium or lead acetates, oxides of bismuth, barium or lead silicates of sodium, calcium or lead, and lead salts of substituted phenols
- such as para-tertiary butyl phenol. Materials such as lead silicate, basic white lead, calcium stearate and lead stearate may be used where clarity or non-toxicity are not of importance.
- The modified vinyl plastisols of the present invention can contain the pigments, fillers and extenders conventionally employed in such compositions.
- In the epoxy resin modifying system, the components are normally present in the proportions of 90 to 120 parts of epoxy resin, 6 to 12 parts of dicyandiamide and 0.2 to 0.6 parts of benzyl dimethylamine. The preferred proportions are 100 parts of epoxy resin, 10 parts of dicyandiamide and 0.4 parts of benzyl dimethylamine.
- The epoxy resin modifying system is normally added to the vinyl plastisol in an amount of 20 parts to 100 parts per 100 parts of the vinyl resin content in the plastisol. The preferred proportions are 40 parts of epoxy resin modifying system to 100 parts of vinyl resin.
- The proportions of vinyl resin to plasticiser in the plastisol can obviously be varied over a wide range depending on the particular properties desired. The relative proportions of the components are well-known to those skilled in the art and the particular amounts to be employed for particular purposes can readily be determined by those working in this field. However, as a rough rule-of-thumb guide, it can be stated that a generally useful proportion of plasticiser is of the order of 50% of the vinyl resin content by weight.
- The particular sequence of combining the components in preparing the epoxy resin modified vinyl plastisols of the present invention is not critical. However, it has been found most practical to prepare a vinyl resin dispersion, admix this with a dispersion of the pigments employed in a suitable plasticiser and then add the epoxy resin modifying system. Further additives, if desired, can be incorporated into the plastisol by conventional means. To ensure thorough blending of all of the components the mixture can be passed through a three-roll mill.
- As an example of a suitable composition of the invention there may be quoted a composition comprising 100 parts by weight of polyvinyl chloride resin, 50.4 parts by weight of dioctyl phthalate, 3 parts by weight of epoxidised soybean oil, 2.5 parts by weight of stabiliser, 1.0 parts by weight of thixotropic agent, 36.8 parts by weight of liquid epoxy resin, 3.7 parts by weight of dicyandiamide, 0.15 parts by weight of benzyl dimethylamine, 8.1 parts by weight of titanium dioxide and 27.0 parts by weight of calcium carbonate.
- The following Example illustrates the invention. The parts referred to are parts by weight.

EXAMPLE

A coating composition according to the present invention is prepared by mixing the following components to form composition A

5	Composition A	Parts
	Geon 121 ¹	100.0
	Diocetyl phthalate	45.0
	Epoxidised soybean oil (Paraplex G-62)	3.0
10	Barium cadmium soap (light stabiliser)	2.0
	Zinc soap (heat stabiliser)	0.5
	Bentone 27 (thixotropic agent)	1.0

¹A polyvinyl chloride resin having a particle size of 44 to 74 microns, a specific gravity of 1.4, and a bulk density of 20—25 pounds per cubic foot and which is designed for dispersion as a plastisol.

Composition A is then combined by hand mixing with a dispersion of 8.1 parts of rutile titanium dioxide in 5.4 parts of dioctyl phthalate.

A blend of 36.8 parts of Araldite 6010 [a liquid epoxy resin having an epoxy value of

0.53 equivalents/100 gms., a specific gravity of 1.17 at 25°C and a viscosity of 12—16,000 cps at 25°C on the Brookfield Viscometer, prepared by reacting 4',4 - dihydroxy - diphenyl propane and epichlorohydrin in a molar ratio of about 1 to 8] 3.7 parts of dicyandiamide and 0.15 parts of benzyl dimethylamine is prepared by admixing the components.

This blend is then added to the vinyl resin-pigment dispersion and then 27.0 parts of calcium carbonate are added. The combination of the above ingredients is thoroughly mixed and blended together by being passed twice through a three-roll mill.

The resulting composition is then spread with a doctor blade onto steel panels, the surfaces of which have been cleaned with trichloroethylene. Similar compositions are prepared using varying amounts of benzyl dimethylamine so that three compositions having 0.2, 0.4, 0.6 parts benzyl dimethylamine per hundred parts of epoxy resin are obtained. The coated panels were then heated in an electrically-heated, mechanical convection oven for 15 minutes at 190°C. The coating obtained had the properties shown in the table below.

Benzyl Dimethylamine content (parts per hundred parts resin)	Adhesion	Colour	Flexibility	Resistance	
				Water	Gasoline
0.2	Fair	Good	Good	Satisfactory	Satisfactory
0.4	Good	Good	Good	"	"
0.6	Excellent	Good	Good	"	"

Tests carried out on panels coated with a composition according to the above example which had been stored on a shelf for three-months showed that the coatings had the same good properties when using the stored composition as when made from the freshly prepared composition.

The words "Araldite", "Bentone", "Geon" and "Paraplex" used herein are registered Trade Marks.

WHAT WE CLAIM IS:—

1. An epoxy resin composition comprising an epoxy resin, dicyandiamide and benzyl dimethylamine.

2. An epoxy resin composition according to claim 1 wherein the epoxy resin is liquid at room temperature.

3. An epoxy resin composition according to claim 1 or 2 wherein the epoxy resin is a polyglycidyl ether prepared from 2,2 - bis(4 - hydroxyphenyl)propane.

4. An epoxy resin composition according to claim 3 where the polyglycidyl ether is pre-

pared by the reaction of 2,2 - bis(4 - hydroxyphenyl)propane with epichlorohydrin.

5. An epoxy resin composition according to any one of the preceding claims which comprises 90 to 120 parts by weight of epoxy resin, 6 to 12 parts by weight of dicyandiamide and 0.2 to 0.6 parts by weight of benzyl dimethylamine.

6. An epoxy resin composition according to claim 5 which comprises substantially 100 parts by weight of epoxy resin, 10 parts by weight of dicyandiamide and 0.4 parts by weight of benzyl dimethylamine.

7. An epoxy resin composition according to claim 1 substantially as described herein.

8. A composition which comprises a dispersion of a vinyl chloride resin in a liquid plasticiser for polyvinyl chloride and an epoxy resin composition as claimed in any one of claims 1 to 7.

9. A composition according to claim 8 wherein the polyvinyl chloride has a molecular weight of 20,000 to 30,000 as measured by the Staudinger method.

10. A composition according to claim 8 or 9 wherein the polyvinyl chloride resin has a particle size of 44 to 77 microns.
- 5 11. A composition according to any one of claims 8 to 10 which comprises 20 to 100 parts by weight of epoxy resin composition per 100 parts by weight of polyvinyl chloride resin.
- 10 12. A composition according to claim 11 which comprises substantially 40 parts by weight of epoxy resin composition per 100 parts by weight of polyvinyl chloride resin.
13. A composition according to any one of claims 8 to 12 which also contains a pigment.
- 15 14. A composition according to claim 8 which comprises 100 parts by weight of polyvinyl chloride resin, 50.4 parts by weight of dioctyl phthalate, 3 parts by weight of epoxidised soybean oil, 2.5 parts by weight of stabiliser, 1.0 parts by weight of thixotropic agent, 36.8 parts by weight of liquid epoxy resin, 3.7 parts by weight of dicyandiamide, 0.15 parts by weight of benzyl dimethylamine, 8.1 parts by weight of titanium dioxide and 27.0 parts by weight of calcium carbonate.
- 20 15. A composition according to claim 8 substantially as hereinbefore described.
- 25 16. A metal surface which has been coated with a composition according to any one of the claims 8 to 15 and then the composition has been cured at an elevated temperature.
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